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THE ADIABATIC AIR DRYING OF HYGROSCOPIC SOLIDS¹

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In this paper experimental data are reported on the adiabatic air drying of hygroscopic solids. The experiments were carried out on slabs of paper pulp and of asbestos. An analysis of the process of drying such solids is given, in which existing conceptions of the mechanism of drying are utilized freely. These concepts are modified somewhat, however, in order that the experimental results might be explained more adequately. The present paper is restricted to the adiabatic case where the bulk of the heat required for the drying process comes from the sensible heat of the drying air, and where the air conditions are constant. As usual in such work, the drying took place from the faces, and was repressed on the edges.

PREVIOUS WORK

The most important investigations on drying theory are those of Lewis (4) and Sherwood (10, 11).

It is unnecessary here to elaborate on the experimental work that has been carried out on the subject, or on the hypotheses that have been advanced to explain the experimental data. It will suffice to note that when the instantaneous drying rate of a solid subjected to constant air conditions is plotted against the instantaneous moisture content of the solid it is found that, in the general case, at high moisture contents the rate is constant; that below a certain critical moisture content the rate of drying decreases with decreasing moisture content and approaches zero at the equilibrium moisture content where the solid is in equilibrium with the drying air; that during the constant rate interval, and during the first stage of the falling rate interval, the air velocity has an important effect

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on the drying rate; and that during the last stages of the falling rate interval the air velocity has little or no effect on the rate of drying.

The mechanism that has been proposed as an explanation of the above facts is, in its essentials, as follows: during the constant rate interval the solid is so wet that it can deliver liquid water to the surface as fast as evaporation can take it away, and the process is essentially the same as that of non-boiling evaporation from a liquid water surface. At the critical water concentration the moisture transferring ability of the solid diminishes to such an extent that water cannot be delivered to the surface fast enough to keep up with the rate of evaporation of the constant rate interval. As a result, the rate of drying decreases. It is assumed that the decrease in rate is accompanied by either a drying out of part of the surface, the remaining part remaining wet, or by a retreat of the zone of vaporization into the solid. As the solid continues to dry, it is further assumed that the rate of water diffusion becomes so slow that it is the controlling reaction. Equations based on the assumption that the rate of moisture diffusion across any plane is proportional to the moisture concentration gradient perpendicular to that plane have been applied to this case, and have been quite successful in describing the drying of non-porous, slow-drying solids such as wood (10, 15) and soap (1, 10).

Lewis, McAdams, and Adams (5) have presented data on the drying of fiber board and pulp and Pukall (8) on the drying of clays. It is shown that, in all probability, the zone of vaporization retreated into the sheet during the falling rate interval.

CLASSES OF WATER PRESENT IN A HYGROSCOPIC SOLID

In previous discussions of drying rate, an important characteristic of the solid, namely, its hygroscopic or moisture-binding power, has not been adequately treated. It has long been recognized, it is true, that if air of definite humidity and temperature is used in a drying process there is a definite equilibrium moisture content which is not removable by that air. On the other hand, the influence of hygroscopic moisture on the mechanism of drying has not been described. This type of moisture plays an important part in the drying of hygroscopic solids.

The vapor pressure of water over a very wet solid is that of liquid water at the temperature of the solid. If water is progres-

sively removed from the solid, a moisture concentration will be reached where the aqueous vapor pressure over the solid begins to decrease and becomes less than that over water at the same temperature. Materials that have a considerable moisture content at this point are hygroscopic solids. These facts suggest that the total water content of a wet solid be divided into two classes: free and bound.⁴ Free water is defined as the water in the solid that exerts its full vapor pressure, and bound water is moisture in the solid that exerts less than its normal vapor pressure. Physically, free water is held in the voids of the solid. Bound water may exist in several conditions: liquid water in very fine capillaries will exert an abnormally low vapor pressure because of high concave curvature; moisture in cell or fibre walls may suffer a vapor pressure lowering because of solids dissolved in it; water in natural organic structures is in physical and chemical combination, the nature and strength of which vary greatly with the nature and moisture content of the solid. For the purpose at hand it is unnecessary to differentiate among these different waters, but simply group them and call the total, bound water.

The relationship between the vapor pressure of water over the solid and the moisture content of the solid is determined by experiment, and is usually given in the form of a curve wherein the moisture content of the material is plotted against the relative humidity of air in equilibrium with the material. The moisture content corresponding to a relative humidity of 100 per cent is the moisture concentration that divides the free and bound waters. If the material is wetter than this, it contains some free water and a maximum amount of bound water. If the material is drier than this, it contains only bound water.

Since the moisture content-relative humidity curve is an equilibrium curve, the same curve should, theoretically, represent the end points of both water absorption and water desorption processes applied to the material. When both absorption and desorption curves have been obtained experimentally, however, the curves do not coincide, but the desorption curves give higher moisture contents for a given relative humidity than do the absorption curves. Desorption curves should be used when drying is under consideration.

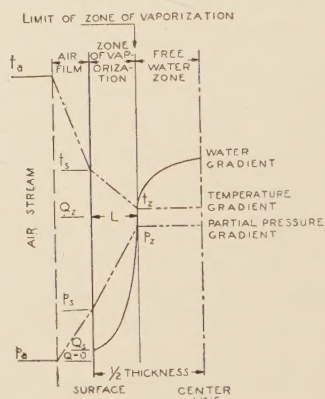
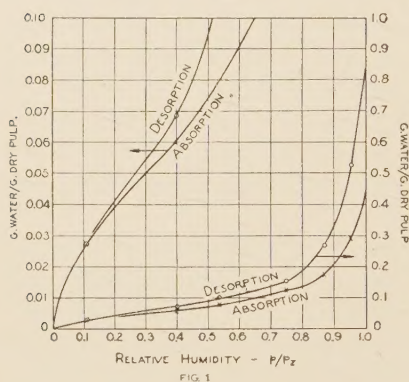
⁴ Many investigators have distinguished between the classes of water in a solid using terms such as, free, pore, surface, capillary, hydration, and hygroscopic.

Figure 1 shows absorption and desorption curves for paper pulp (9).

The moisture content of the material that corresponds to the relative humidity of the air used in the drying is a point on the desorption curve. This is the usual "equilibrium moisture content," and is entirely bound water.

SUGGESTED MECHANISM OF THE DRYING OF HYGROSCOPIC SOLIDS

The mechanism of drying during the constant rate interval is well established, and has been described above. The mechanism during the falling rate interval, however, is still open to discussion.



The following assumptions are made:

1. Under ordinary drying conditions only free water diffuses through the solid as liquid water, and when bound water is transferred it is transferred as vapor. This does not imply that bound water cannot diffuse as liquid, but it does suggest that the rate of such diffusion is slow in comparison with that of free water.
2. When water vapor is diffusing through the solid, the material at any point in the path of the vapor is in equilibrium with vapor, where the equilibrium is shown by the desorption curve of the material.

Since the rate of drying decreases after the critical water concentration is reached, the partial pressure gradient in the air adjacent to the solid decreases. Also, since the heat required for the vaporization of the water decreases, the temperature gradient in this air also decreases. Up to the critical water concentration the

air at the air-solid interface is saturated. If the humidity at the interface decreases and the temperature increases, the air at the interface becomes unsaturated, and can be considered a mixture of air and superheated steam. This indicates, first, that either free water must have been vaporized before it reached the surface,⁵ or that, if vaporization at the interface is occurring, it must be from bound water; and second, that at the critical point the concentration of moisture at the surface equals the equilibrium moisture concentration corresponding to saturated air at the temperature of the solid-air interface. During the constant rate interval, in the absence of transfer of heat by radiation, or by conduction through the solid, the temperature of the solid will be that of the wet bulb temperature of the air (II).

As the drying process goes on, the temperature at the surface continues to rise, and the partial pressure at the surface continues to fall. This indicates that if vaporization of free water is occurring such vaporization is taking place at a constantly increasing distance from the surface. A detailed description of the process at such a stage is of interest. The discussion can be followed with the aid of Fig. 2 which shows, diagrammatically, conditions in one-half of the slab during the period when vaporization is occurring well within the solid, but before the free water has been entirely removed from the center portion of the solid. In Fig. 2 distances perpendicular to the drying surfaces are plotted as abscissas, and local temperatures, pressures, and moisture contents as ordinates. During this period, the half-slab is divided into two zones; a vaporization zone in which water is vaporizing and in which only bound water is present; and a free water zone in which both the free water and the maximum quantity of bound water are present. Free water cannot exist in the vaporization zone, as it would be at a higher temperature and vapor pressure than the water in the free water zone, and conse-

⁵ If the surface of the solid is mat there will be a true "unsaturated surface" drying period characterized by the appearance of a dry network of solid. This concept has been quite strongly emphasized (II, 4). Such a condition will persist for a certain time, the length of which should be short under ordinary drying conditions. Lewis, McAdams, and Adams (5) have shown that conditions during such a period are complicated. In this connection it would seem that a vaporization zone entirely inside the solid but only a short distance below the surface would satisfy all of the criteria of the so-called unsaturated surface drying period.

quently would diffuse as water vapor to the free water zone. Free water is diffusing to the limit of the zone of vaporization and is vaporizing at or near this plane. All through the zone of vaporization bound water is vaporizing, so that, as the stream of water vapor diffuses toward the surface, it is augmented by vaporized bound water. The partial pressure gradient is represented by the line $p_z - p_s - p_a$. A partial pressure difference $p_z - p_s$ over the vaporization zone provides driving force for the vapor diffusion process. At any point in the vaporization zone the air is in "equilibrium" with the solid, as represented by the desorption curve that corresponds to the conditions of the drying process. It is apparent here that the hygroscopic properties of the solid play an important part in the drying mechanism; if the solid is non-hygroscopic, vaporization is confined to a narrow zone inside the solid, whereas if the material is hygroscopic, a considerable portion of the evaporation takes place between the surface and the limit of the zone of vaporization (16).

The driving force for the heat transfer through the air resistance is the temperature difference $t_a - t_s$, and that for heat flow to the limit of the vaporization zone is the temperature difference $t_s - t_z$. If the solid is hygroscopic, not all of the heat must flow through the entire vaporization zone, since some of it is utilized for evaporation between the surface and the limit of the vaporization zone.

If the solid is not hygroscopic, i.e., if it has a negligible bound water content even when in contact with saturated air, the above mechanism is simplified, but not changed in its essentials. The vaporization takes place in a relatively narrow zone, and as this zone moves into the interior of the solid it leaves dry solid behind it (11).

When the limit of the zone of vaporization reaches the center line of the slab, the free water is entirely gone. The rest of the drying process is concerned with the removal of the bound water that remains in the slab after the free water is removed.

If the solid is non-hygroscopic, the process is terminated when the limit of the zone of vaporization reaches the center line of the slab.

Differential Equations for the Drying Process During the Falling Rate Interval

Based on Fourier reasoning, two partial differential equations can be derived that apply to the mechanism of drying given above.

One of the equations applies to the diffusion of the water vapor, and the other to the flow of heat. Both equations only apply where there is no free water present, that is, in the zone of vaporization.

Let it be assumed that the weight rate of water vapor diffusion per unit surface area is proportional to the partial pressure gradient normal to the surface. By writing a moisture balance over a thin slice of the solid cut perpendicularly to the direction of diffusion, it can be shown that ⁶

$$D \frac{\partial Q}{\partial \theta} = \frac{\partial}{\partial L} \left(k_m \frac{\partial p}{\partial L} \right). \quad (1)$$

In general, k_m varies with Q , because of shrinkage. Also, the bound water content is a function of the relative humidity and, to some extent, of temperature, so

$$Q = f(p/p_s, t) \quad (2)$$

and

$$k_m = \varphi(Q). \quad (3)$$

To integrate Equation (1) in the general case, the functional relationships of Equations (2) and (3) must be determined and utilized, and the usual boundary conditions specified. One of the boundary conditions must account for a variation in the limit of L , which depends, in turn, on conditions in the free water zone.

The corresponding equation for heat flow is

$$D \left[c(1 + Q) \frac{\partial t}{\partial \theta} - r \frac{\partial Q}{\partial \theta} \right] = \frac{\partial}{\partial L} \left(h_m \frac{\partial t}{\partial L} \right). \quad (4)$$

Appropriate boundary conditions must be specified for Equation (4).

It is immediately apparent that, to integrate Equations (1) and (4) is, for the general case, hopeless. The equations are not independent, since Q depends on p/p_s and t . A special case, however, is of interest.

Consider the slow drying of a non-porous solid under such conditions that these assumptions can be made:

1. The vapor diffusion resistance is so high in comparison with the heat flow resistance that the slab remains at nearly constant temperature. Then t and p_s are constants.

2. The diffusion coefficient, k_m , is constant. This assumes negligible shrinkage.

⁶ A table of nomenclature is given at the end of the paper.

3. The relationship between Q and p/p_z is linear, so

$$Q = \frac{a}{p_z} p + b \quad (4)$$

and

$$\frac{\partial Q}{\partial \theta} = \frac{a}{p_z} \frac{\partial p}{\partial \theta} \quad (5)$$

4. The slab contains no free water so that the equation can be integrated over a constant half-slab thickness.

On the basis of these assumptions Equation (1) simplifies to

$$D \frac{\partial Q}{\partial \theta} = \frac{k_m p_z}{a} \frac{\partial^2 Q}{\partial L^2} = J \frac{\partial^2 Q}{\partial L^2} \quad (6)$$

Equation (6) is of the same form as that derived by assuming that the moisture moves through the solid by liquid diffusion, and that the rate is proportional to the moisture concentration gradient. The only difference is that in place of the constant J of Equation (6), there occurs the coefficient of diffusion of liquid water through the solid. The integrations have been carried out by a number of investigators (1) (6) (7) (10) (15) for various boundary conditions. It is obvious that such integrated equations should apply to either mechanism—liquid diffusion, or vapor diffusion under the four restrictions given above. It is interesting to note that experimental data used to verify the integrated equations were obtained under conditions that conformed approximately to these four restrictions.

Approximate Equations for the Drying Process During the Falling Rate Interval

Approximate equations can be derived for the case where the solid possesses negligible bound water and where it be assumed also that the thermal conductivity and vapor diffusivity are constant throughout the zone of vaporization; and that thermal effects other than latent heat of water are small.

The following equations can be written

$$\begin{aligned} (p_s - p_a)k_g &= \left(\frac{p_z - p_s}{L} \right) k_m = w_f \\ &= \left(\frac{t_a - t_s}{r} \right) h_g = \left(\frac{t_s - t_z}{rL} \right) h_m. \quad (7) \end{aligned}$$

Define the ratios α_g and α_m by the equations:

$$\alpha_g = h_g/k_g \quad \alpha_m = h_m/k_m, \quad (8)$$

and the overall coefficients of heat and water transfer by the equations:

$$\left. \begin{aligned} U &= \frac{1}{1/h_g + L/h_m} \\ K &= \frac{1}{1/k_g + L/k_m} \end{aligned} \right\}. \quad (9)$$

From equations (7), (8) and (9) it follows that

$$\frac{p_z - p_a}{t_a - t_z} = \frac{1/k_g + L/k_m}{r(1/h_g + L/h_m)} = \frac{\alpha_g \alpha_m (k_m + Lk_g)}{r(h_m + Lh_g)} = \frac{U}{Kr}. \quad (10)$$

Let

$$\alpha_m/\alpha_g = C. \quad (11)$$

Then

$$\frac{p_z - p_a}{t_a - t_z} = \frac{\alpha_g(k_m + Lk_g)}{r(k_m + Lk_g/C)} = \frac{U}{Kr}. \quad (12)$$

For constant drying conditions, p_a and t_a are constant. The partial pressure p_z is a function of temperature, t_z , since the air is saturated at the limit of the vaporization zone. When t_z increases p_z also increases.

From Equation (12) certain interesting conclusions can be drawn. If $C > 1$, $(p_z - p_a)/(t_a - t_z)$ increases as L increases. This requires that p_z and t_z increase, and a certain amount of heat must flow by conduction into the free water zone. If $C > 1$, therefore, the temperatures in the free water zone should increase with time.

If $C < 1$, $(p_z - p_a)/(t_a - t_z)$ decreases as L decreases. This requires that p_z and t_z decrease, so the temperature of the free water zone should decrease with time.

For the special case where $C = 1$, t_z should remain constant.

By eliminating p_s and t_s from Equation (7):

$$k_g = \frac{w_f}{p_z - p_a - \frac{w_f L}{k_m}} \quad (13)$$

and

$$h_g = \frac{r w_f}{t_a - t_z - \frac{r L w_f}{h_m}}. \quad (14)$$

Dividing Equation (13) by Equation (14) and solving for L :

$$L = \frac{k_m C(p_z - p_a) - \frac{h_m}{r}(t_a - t_z)}{w_f(C - 1)} \quad (15)$$

Study of Equation (15) in the light of Equation (12) shows that L increases as w_f decreases. At the start of the falling rate period (critical point) L is zero,

$$w_f = k_g(p_s - p_a) = k_g(p_z - p_a) \quad (16)$$

and

$$w_f = \frac{h_g(t_a - t_s)}{r} = \frac{h_g(t_a - t_z)}{r} \quad (17)$$

Whenever w_f falls below the value given by Equations (16) and (17) L becomes positive and the zone of vaporization moves into the solid.⁷

If the solid is hygroscopic, the above equations do not apply quantitatively, due to the complications mentioned in the discussion of the differential equations of the drying process. It seems clear, however, that the qualitative deduction from Equations (15), (16), and (17) still holds true; namely, when w_f decreases below a certain critical value, the limit of the zone of vaporization begins to move into the solid, and, other things being equal, the faster the decrease of w_f , the faster the increase in L .

EXPERIMENTAL

Most of the experiments were carried out on slabs of paper pulp. A few runs were made on asbestos to compare the mechanism of the drying of a relatively non-hygroscopic material with that of a hygroscopic solid.

The purpose of the first, and most important, series of runs was to show, by experiment, the mechanism of the drying of such solids. In this series, the porosity was varied from run to run, by changing the fiber size.

⁷ Equation (15) fails for the special case $C = 1$. For this case Equation (7) can be written:

$$L = \frac{k_m(p_z - p_s)}{w_f} \quad (15a)$$

$$L = \frac{h_m(t_s - t_z)}{rw_f} \quad (15b)$$

When w_f becomes less than that given by Equations (15a) and (15b) p_s decreases, t_s increases, and L becomes positive.

Later runs, in which the data taken were not so complete, were made in order to show directly the effects on the drying rate curve of the important drying variables, such as the slab thickness, the density of the solid, and the temperature, humidity, and velocity of the air.

Procedure

The samples used in the drying experiments were fabricated from raw fiber stock. Separate plies were made on a laboratory paper sheet mold and the plies comprising the test sample were firmly pressed together. The edges of the samples were heavily coated with collodion to prevent escape of water vapor from the edges of the sample.

The drying samples, suspended from the arm of a balance, hung in a stream of conditioned air. The drying air was conditioned by water sprays and heating coils, both under automatic control. The air stream was turbulent and as the drying sample was continually turned, the air conditions at all points on the sample were uniform. A semi-precision potentiometer was used to measure the potential of the thermocouples.

The most important data taken were a weight loss vs. time curve on the drying sample, and were obtained by noting the time required for the balance to trip at reduced weight settings of two grams. The time required to evaporate two grams of water from the sample was plotted versus the total water in the solid and a curve drawn through the points. The instantaneous rates of drying at average water concentrations of the sample were readily calculated from this curve, and the drying rate curve plotted. This method of obtaining the drying rate curve was found to be more accurate than differentiating a weight vs. time curve.

To establish the mechanism of the drying of the pulp, it was necessary to evaluate, in addition to the drying rate itself, the rates of heat and water vapor transfer, and the gradients of temperature and moisture concentration at various periods during the process. In the first series of runs, therefore, the drying samples were built of fourteen uniform plies of pulp. Copper-constantan thermocouples composed of 32 gauge enamelled wire, were inserted between the plies, and surface thermocouples were placed under thin plies 0.002 in. thick. The assemblies were pressed to form compact and uniform samples. The slabs were 17×17 cm., so at least 8 cm. of each thermocouple lead was in an isothermal plane. Similar

samples, without thermocouples, were used to obtain water concentration gradients; the samples were removed at various times during the drying process, and the plies separated and analyzed for water.

The shrinkage of the samples during drying was determined by measuring the thicknesses of the individual plies.

The slabs used in later experiments were prepared of two plies with a thermocouple between the plies. This thermocouple was for the purpose of measuring the lowest temperature (t_z) in the slab.

RESULTS AND DISCUSSION

The results obtained in Runs 101K, 104K, and 102K will first be discussed. The data of Run 101K will be treated in considerable detail, since these data present an experimental confirmation of the essential points of the drying mechanism under discussion. Runs 104K and 102K, in addition to giving checks on the mechanism, show the effect on the drying rate of decreasing the porosity of the pulp slabs.

Mechanism of Drying, as Shown by the Drying of a Porous Pulp Slab

The data from a drying experiment carried out with a very porous pulp slab are plotted in Fig. 3. These data are from Run 101K. The abscissas of all of the curves are the average water concentrations in grams of total moisture per gram of dry pulp. The ordinates of the various curves are:

Rate of drying—Loss of moisture in grams per hour per square centimeter of drying area.

Temperatures—The temperatures in the slab as measured by thermocouples 1 to 4, located, respectively, at 1.5, 28, 57, and 85 per cent of the distance from the surface to the center line.

The overall heat transfer coefficient, U —This coefficient was calculated from the Equation:

$$U = \frac{Sr}{t_a - t_z}, \quad (18)$$

using as t_z the temperature recorded by thermocouple 4.

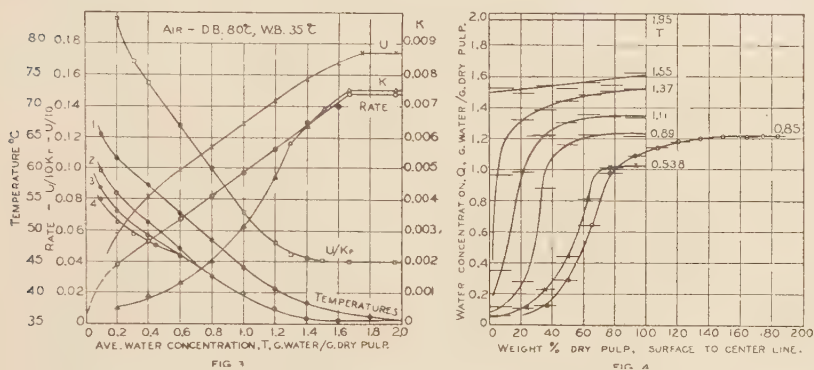
The overall vapor diffusion coefficient, K —This coefficient was calculated from the Equation:

$$K = \frac{S}{p_z - p_a}, \quad (19)$$

using as p_z the vapor pressure of water at temperature t_z .

The ratio U/Kr —This is the heat-diffusion ratio introduced in Equation 10.

In Fig. 4, the water concentrations in the slab during the drying process are plotted as ordinates vs. distances from the surface as abscissas. The numbers at the righthand ends of the curves are the average water concentration of the entire slab. The single extended curve is for another slab, identical in structure, and dried under the same conditions, but 1.9 times as thick as the sample under discussion.



Study of Fig. 3 shows that the drying of the slab can be divided into four periods:

Period 1 where $T > 1.67$. During this period everything remained constant except the moisture concentration. This is the usual interval of constant rate drying. The temperature of the slab was the wet bulb temperature of the air. The critical concentration, where the rate began to fall, was $T_{cp.} = 1.67$.

Period 2 where $1.67 > T > 1.40$. During this period the rate of drying, and the overall coefficients U and K decreased. The lowest temperature in the slab remained at the wet bulb temperature of the air, but the surface temperature increased slightly, as did the ratio U/Kr . The decreases in U and K indicate an increase in the average length of path of heat and moisture flows, which shows that the limit of the zone of vaporization has retreated to some extent into the slab. This is not inconsistent with the small changes noted in surface temperature and in the ratio U/Kr . Reference to Equation (12) shows that if L is small, the ratio U/Kr is not greatly affected by the value of L , as the larger portion of each of the quantities $(p_z - p_a)$ and $(t_a - t_z)$ is over the air-side resistance.

Visual observation of the surface indicated that it was dry immediately after the critical water concentration, but this is not indicated by the water gradient (Fig. 4) at $T = 1.55$, because the sample could not be removed from the drier and the plies separated quickly enough to prevent the transfer of free water to the surface.

Period 3 where $1.40 > T > 0.40$. During this period, the rate of drying, and the coefficients U and K continued to decrease. The decreases in these coefficients indicate that the length of path of heat and moisture flow continued to increase, and that the zone of vaporization continued to penetrate more deeply into the slab. The ratio U/Kr increases at an appreciable rate. This shows, first, that the resistances in the slab are now becoming important in comparison with those in the air film, and, second, that C for this case must be greater than unity. (See Equation 12.)

The temperatures of the outer layer of the slab increased during this period. The temperature gradient in the slab became more pronounced. From $T = 1.4$ to $T = 0.73$, the temperature gradient extended from the surface to the location of the second thermocouple. The temperature gradient penetrated more deeply as the process went on, and reached the location of the fourth thermocouple when $T = 0.55$. The limit of the zone of vaporization may be located approximately by the inside end of the temperature gradient. For example, from Fig. 3, when $T = 0.60$ the temperature gradient extended to the location of the third thermocouple, which was placed about 60 per cent of the distance from the surface to the center line. From Fig. 4, it is to be noted that, when $T = 0.60$, the moisture concentration at a plane 60 per cent of the distance from the surface to the center line is between 0.80 and 1.00 parts of water per part of dry pulp. This is approximately equal to the bound water concentration of the pulp in contact with saturated air, as shown in Fig. 1. It is further noticed that the temperature at the limit of vaporization tends to rise. As shown in the discussion of Equation (12) this is consistent with a value of C greater than unity. It will be shown later that the numerical values of h_g/k_g , and h_m/k_m are such that C is between 3 and 5.

The moisture gradients show that the surface of the slab was definitely dry during the third period.

Period 4 where $0.40 > T > 0$. During this period the rate of drying decreased rapidly. It is evident from Fig. 4, that, at the beginning of this period, the limit of the vaporization zone was near the center surface of the slab. When the vaporization zone reaches

the center, only bound water remains. From this time on, the rate of drying decreased rapidly because the maximum vapor pressure in the slab was no longer a function of the temperature of the free water present, but depended upon the temperature and highest bound water concentration still remaining in the slab.

Estimation of Constant C

From the data shown in Fig. 3 it is possible to obtain an estimate of the coefficients h_g , k_g , h_m , and k_m , and so to obtain a value of C .

The value of h_g is equal to that of U during the constant rate interval, so $h_g = 1.74$ cal./hr. sq. cm. °C.

The value of k_g is likewise equal to that of K during the constant rate interval, so $k_g = 0.0075$ g./hr. sq. cm. mm. Hg.

The ratio $\alpha_g = h_g/k_g$ is, then, $1.74/0.0075 = 230 \frac{(\text{cal.})(\text{mm. Hg.})}{(\text{g.})(^\circ\text{C.})}$.

The most precise determination of this ratio is that of Sherwood and Comings, (13) who found that the analogous ratio, h_g/k_g' equals, for water vapor-air, 2.6. If Sherwood and Comings' ratio is converted to the above units of h_g/k_g , it becomes $300 \frac{(\text{cal.})(\text{mm. Hg.})}{(\text{g.})(^\circ\text{C.})}$, (assuming a partial pressure of water vapor of about 30 mm.) Sherwood and Comings (13) have shown how difficult it is to determine such a ratio with precision, and the value of 230 is not really very inconsistent with Sherwood and Comings' more accurate ratio.

When L , the distance from the surface to the point where $Q_z = 1.0$, was 35 per cent of the halfslab thickness, U was 1.2 cal./hr. sq. cm. °C., and K was 0.00025 g./hr. sq. cm. mm. Hg. Then, since $L = (0.35)(0.370) = 0.130$ cm. substitution in Equation (9) gives:

$$U = 1.2 = \frac{1}{\frac{1}{1.74} + \frac{0.130}{h_m}}$$

and

$$K = 0.00250 = \frac{1}{\frac{1}{0.0075} + \frac{0.130}{k_m}},$$

from which

$$h_m = 0.503 \frac{\text{cal.}}{\text{hr. cm. } ^\circ\text{C.}}$$

and

$$k_m = 0.000488 \frac{\text{g.}}{\text{hr. cm. mm. Hg.}}$$

The above value of h_m agrees well with the value 0.525 obtained by Lees and Charlton (3) on blotting paper. The ratio $\alpha_m = h_m/k_g$ is $0.503/0.000488 = 1050$.

If α_g is taken as 300,

$$C = \alpha_m/\alpha_g = 1050/300 = 3.5 \frac{(\text{cal.})(\text{mm. Hg.})}{(\text{g.})(^\circ \text{C.})},$$

while if α_g is 230

$$C = 1050/230 = 4.6 \frac{(\text{cal.})(\text{mm. Hg.})}{(\text{g.})(^\circ \text{C.})}.$$

It is apparent, therefore, that the value of C is considerably greater than unity.

Effect of Porosity on the Mechanism of Drying

Runs 104K and 102K were made with slabs prepared from beaten paper pulp. The beating process reduced the size of the fiber aggregate. The procedure used, and the data taken, were identical with those of Run 101K, except that, in Run 104K, twice as much pulp was used.

During drying considerable shrinkage took place, and the density of the solid increased. The shrinkage was smallest in Run 101K, and greatest in Run 102K. Accompanying the increase in density was a decrease in porosity, as measured by the ability to transmit air. This decrease in porosity was small in Run 101K, moderately large in Run 104K, and enormous in Run 102K. The slabs used in these runs are compared in Table I.

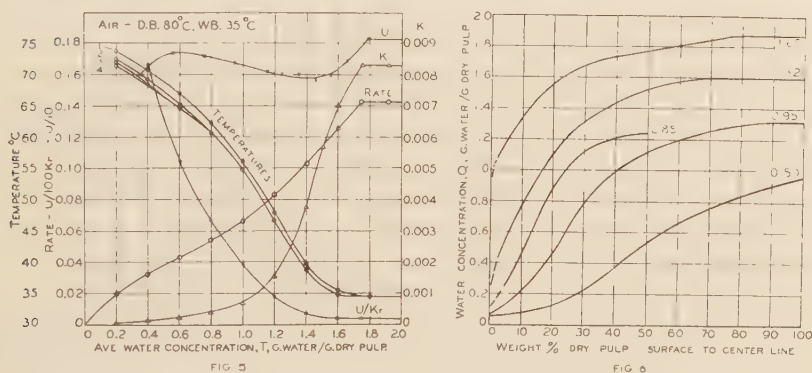
TABLE I
COMPARISON OF SLABS OF RUNS 101K, 104K AND 102K

Run	Per cent Increase in Density of Solid	Final Structure
101K.....	15	Very porous, similar to blotting paper.
104K.....	25	Medium porous, similar to writing paper.
102K.....	60	Non-porous, similar to parchment.

Although the decrease in porosity was accompanied by a considerable increase in density, the decrease in porosity was so very great, that Runs 101K, 102K, and 104K show qualitatively the effect of porosity alone.

The drying data of Run 104K are plotted in Fig. 5 and the water concentration gradients of this run in Fig. 6.

The curves for Run 104K are similar to those of Run 101K, in which the very porous slab was used. The most noticeable difference is in the behavior of the overall heat transfer coefficient U . The coefficient decreased somewhat, then increased, and finally decreased. It is not apparent just why U should dip just beyond the critical point, but, at any rate, it remains at a high level until $T = 0.4$. On the other hand, the overall diffusion coefficient K decreases rapidly immediately after the critical point. The difference in the behavior of U and K is explained by the fact that, as porosity decreases, the thermal conductivity h_m of the slab increases and the diffusion coefficient, k_m , decreases, while h_0 and k_0 remain unchanged. As a result, the relative importance of the term L/h_m of Equation (9) is decreased, and that of the term L/k_m of the



same equation is increased, so K is much more sensitive to increasing L than is U . It will also be noted that the temperature drop in the solid is considerably less than was the case in Run 101K. This is because with the higher value of h_m , a smaller proportion of the total temperature drop is required to drive heat through the vaporization zone.

The rate of drying and coefficient curves for the very non-porous slab of Run 102K are shown in Fig. 7, and the moisture gradients during the run in Fig. 8. No constant rate period appears in the curves, but this is due to the fact that the original surface area of the slab was used in the rate computation, in spite of the fact that the sample shrank considerably and curled at the edges. Approximate correction indicated that a constant rate existed until T was between 1.1 and 1.2. As there were only small differences among

the temperatures indicated by the thermocouples in the slab, only two temperatures are plotted; the lowest temperature in the slab and the temperature at the surface. In general, the differences between Runs 101K and 104K were magnified in Run 102K.

A porous asbestos slab, Run 103A, was dried with the same procedure and conditions as the pulp slabs, and the resulting curves are so similar to those of Run 101K, that it is unnecessary to reproduce them.

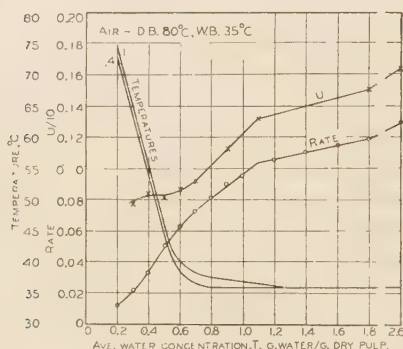


FIG. 7

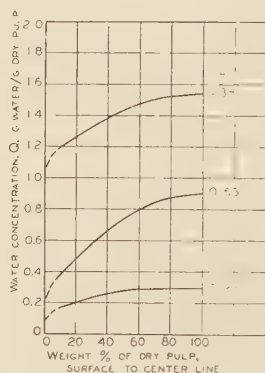


FIG. 8

Effect of Operating Variables on Drying Rate Curves

Special runs were made to determine experimentally the effects of these variables on the drying rate curves: thickness of slab, the density of the slab, and the temperature, humidity and velocity of the air stream. The slabs used in these runs were each prepared of two similar plies, with a thermocouple between the plies. Paper pulp and asbestos slabs were used. The properties of the slabs, the drying air conditions, and other pertinent data obtained in these runs are given in Table II. The second column of Table II gives the air velocity. The actual velocity was not determined, but characterized under three heads—"low," "normal" and "high." Columns three and four give the dry and wet bulb temperatures of the air; columns five and six the thickness before and after drying; columns seven and eight give the edge dimensions before and after drying; column nine gives the dry weight of the slab; column ten the initial dry density; column eleven the critical water concentration; column twelve the rate of drying at the critical point; and the last column the free water concentration at the critical point. The data in this last column will be discussed later in this paper.

TABLE II
DRYING DATA ON ALL SLABS

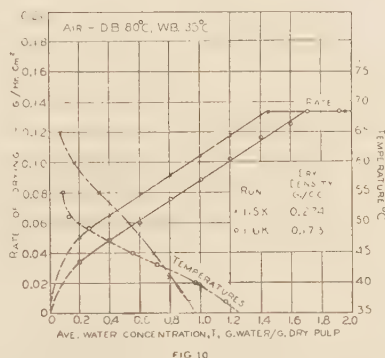
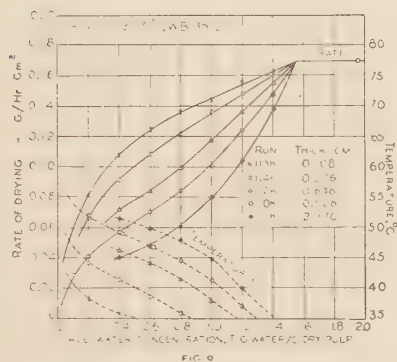
Run	Air Conditions		Thickness		Edge Dimension Square Sample		Wt. of Dry Material g.	Dry Density Wet Basis g./cc. Dry Material	Avg. Water Conc. at Critical Point g./g. Dry Material	Rate of Drying at Critical Point g./hr. cm. ²	Free Water Concentration at Critical Point f_{cp} g./cc.	
	Velocity (Relative)	t_{DB} °C.	t_{WB} °C.	Thickness		Edge Dimension Square Sample						
				Initial cm.	Dry cm.	Initial cm.						Dry cm.
Pulp Runs												
101K	Normal	80	35	0.737	17	17	51					
102K	"	80	35	0.825	17	17	47					
104K	"	80	35	1.25	17	17	93					
110K	"	80	36	0.988	17	17	72					
111K	"	80	36	2.37	17	17	172					
112K	"	80	36	0.648	17	17	47.3					
113K	"	80	36	0.108	17	17	7.94					
114K	"	80	36	0.276	17	17	20.1					
115K	Low	80	36	0.560	17.3	17	46	0.251	1.55	0.17	0.138	
116K	"	80	36	0.890	17	16.5	44.6	0.251	1.55	0.17	0.138	
117K	"	80	36	0.570	17.3	17	47.1	0.251	1.55	0.17	0.138	
118K	Normal	80	36	0.635	16.8	16	30	0.251	1.55	0.17	0.138	
119K	"	80	36	1.270	16.8	16	59.7	0.274	1.45	0.133	0.123	
120K	"	80	36	0.380	16.3	16.3	47.8	0.173	1.71	0.133	0.121	
121K	"	80	36	0.635	17.1	16.8	42	0.275	1.45	0.132	0.124	
122K	"	80	36	0.191	16.8	15.8	13.2	0.167	1.75	0.142	0.125	
123K	"	80	50	0.635	17	16.7	61.9	0.167	1.75	0.152	0.125	
124K	"	71	35	0.700	16.7	16.7	66	0.427	1.55	0.147	0.126	
125K	"	72	36	0.880	17.1	16.8	80.6	0.229	1.52	0.140	0.122	
								0.244	1.31	0.108	0.101	
								0.337	1.37	0.117	0.121	
								0.326	1.37	0.117	0.121	
								0.314	1.38	0.116	0.119	

TABLE II—Continued

Run	Air Conditions		Thickness		Edge Dimension Square Sample		Wt. of Dry Material g.	Dry Density Wet Basis g. Dry Material /cc.	Avg. Water Conc. at Critical Point g./g. Dry Material	Rate of Drying at Critical Point g./hr. cm. ²	Free Water (concentration at Critical Point F_{cp} , g./cc.
	Velocity (Relative)	t_{DB} °C.	t_{WB} °C.	Initial cm.	Dry cm.	Initial cm.					
Pulp Runs											
126K	"	55	36	0.880	0.650	17.1	16.3	44.4	1.58	0.053	0.098
127K	"	64	30	0.597	0.520	16.7	16.3	35.7	1.57	0.127	0.121
140K	"	64	30	0.890	0.585	16.9	16.5	64.1	1.51	0.160	0.130
141K	"	84	50	0.825	0.685	16.8	16.5	57.7	1.48	0.151	0.118
143K	"	83	50	0.890	0.710	17.0	16.5	60.5	1.55	0.152	0.130
144K	High	83	50	0.788	0.597	16.9	16.5	53.5	1.60	0.196	0.142
145K	Normal	104	70	0.927	0.700	16.8	16.3	63.5	1.52	0.180	0.145
Asbestos Runs											
103A	Normal	80	36	1.33	0.815	17	16.5	285	0.15	0.27	
150A	High	80	36	0.825		16.5	16.4	228	0.15	0.27	
151A	"	80	36.5	1.230	1.180	16.3	16.1	312	0.15	0.27	
152A	"	80	36.5	0.420	0.407	16.5	16.5	108	0.15	0.27	
153A	"	80	36.5	1.690	1.590	16.7	16.6	458	0.15	0.27	
154A	"	80	36.5	0.458	0.420	16.5	16.5	108	0.146	0.248	
155A	"	80	35.2	1.330	1.21	16.7	16.6	312	0.158	0.243	
156A	Normal	80	36.5	1.330	1.19	16.6	16.3	312	0.155	0.174	
157A	"	70	36.5	1.30	1.19	16.5	16.2	312	0.145	0.120	
158A	"	65	36	1.30	1.19	16.5	16.3	312	0.136	0.095	
159A	"	55	36	1.27	1.17	16.5	16.3	312	0.130	0.064	

Influence of Slab Thickness

Runs 110K to 114K inclusive were carried out with all variables constant except thickness. The results are plotted in Fig. 9. Two families of curves are given: the rate of drying vs. average water concentration of the slab; and the center temperature vs. the average total water concentration. It will be noted that, for a given moisture concentration in the falling rate interval, the thicker the sample, the slower is the drying rate; and the thicker the sample the higher is the center temperature.



These results are entirely consistent with the assumed drying mechanism. For example, consider the conditions in two slabs of different thickness (other variables constant) that are drying at the same rate, during the interval of falling rate drying, but before all the free water is removed. If the rate of moisture loss is the same in the two slabs, the zones of vaporization in each will be identical in all respects, including thickness. The zone of vaporization in the thin slab will be a larger fraction of the total slab than that in the thicker slab. Evidence will be given later showing that the average water concentrations in the free water zones of the two slabs will be nearly equal. The average moisture concentrations in the free water zones are obviously greater than the average concentrations in the zones of vaporization, so at equal rates of drying the thicker slab will have a greater total average water concentration than the thinner one. The abscissa of a point on the drying rate curve depends, therefore, upon the thickness of the slab, and the drying rate curves change from concave downwards for thin slabs to concave upwards for thick slabs.

For example, compare the gradients marked $T = 0.538$ and $T' = 0.85$ in Fig. 4. These two gradients are very nearly the same in the zone of vaporization, and presumably the slabs for which the gradients were determined were drying at substantially the same rate. It is easily seen that the average moisture concentration of the thick slab must be greater than that of the thin.

The temperatures in the slabs increased in the interval of falling rate drying as is predicted by Equation 12 for the case when $C > 1$. In these runs the coefficient C and air conditions were the same for all slabs. From consideration of Equation 7, therefore, when the slabs were drying at equal rates, the limits of the zones of vaporization in the slabs should be equal distances beneath the surfaces of the slabs if the lowest temperatures in the slabs were equal. The lowest temperatures in the slabs at equal rates of drying are given in Table III.

TABLE III
RUNS 110K TO 114K. LOWEST SLAB TEMPERATURES, ° C.

Run	Rate of Drying, g./hr. cm. ²						
	0.17	0.14	0.12	0.10	0.08	0.06	0.04
113K	35	35	35	37	38	41	
114K	35	35	37	40	43	45	
112K	35	35	37	41.5	45	47.5	
110K	35	35	37	41.5	45	48	52
111K	35	35	37	41.0	45	48	52

These data show that at equal rates of drying the limits of the zones of vaporization were at equal distances below the surfaces of the slabs as long as free water was present. The relationship fails when the rate curves for these pulp slabs became concave downwards, which happened when all the free water was removed, and the limit of the vaporization zone had reached the center line.

After the critical point the overall coefficients of heat transfer and water diffusion decreased for all slabs.

Influence of Density of Dry Material

Runs 115K and 116K, the results of which are plotted in Fig. 10, show the effect on the drying rate curves of changing dry density. The slabs used contained equal amounts of pulp, so the thickness of the slabs also varied. The porosities of the slabs used in Runs 115K and 116K were about equal to that of the slab of Run 101K. The

dry density of slab 115K was 0.274 g./cc., and that of slab 116K was 0.173 g./cc. Both slabs suffered equal shrinkage during drying. The most noticeable difference between Runs 115K and 116K is in the critical water concentrations. This difference is discussed later. Comparing the rate curves with those of Runs 110K and 112K in Fig. 9, which cover about the same range of thicknesses, the effect of increasing the dry density is to decrease the critical water concentration and to shift to the left the rate curve of the falling rate interval.

Influence of Relative Humidity and Temperature of Air

In Fig. 11 the drying rate curves of asbestos Runs 156A, 157A, 158A, and 159A are plotted and show the effect of changing the

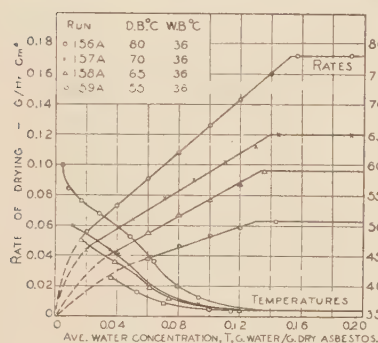


FIG. 11

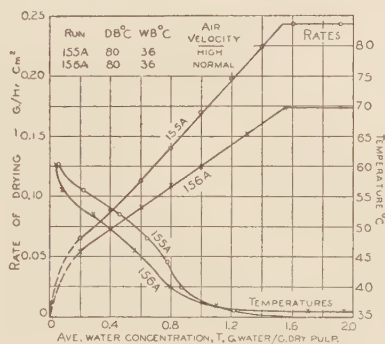


FIG. 12

relative humidity of the drying air. All other variables including the wet bulb temperature of the air, remained constant. The effect of decreasing the relative humidity is to increase the vapor pressure and temperature gradients between the slab and the drying air (11). During the interval of constant rate drying the change in the rate of drying is proportional to the change in the gradients. This proportionality continues throughout the drying process. (See Equation 7.) Thus, as the air humidity is changed, the rate curves in Fig. 11 are displaced vertically in proportion to the rate of drying during the constant rate interval.

In Runs 156A, 157A, 158A, and 159A, the relative humidity was varied by changing the dry bulb temperature of the air. The wet bulb temperature was constant. In Runs 121K, 123K, 127K, 140K, 141K, 143K, 144K, and 145K (see Table II), various wet

bulb temperatures were used, but no appreciable effect of this variation was noted other than the effect of the corresponding changes in relative humidity or dry bulb temperatures.

Influence of Velocity of Air Stream

In Fig. 12 are plotted drying rate curves on asbestos slabs 155A and 156A which were dried with air streams of varying but unknown velocity. All other variables remained constant. A change of air velocity affects only the coefficients k_g and h_g (II). As shown by Equations 16 and 17, the rate of drying during the interval of constant rate drying is directly proportional to the film coefficients, but as shown by Equation 9, the coefficients k_g and h_g are, in the interval of falling rate drying, only parts of the overall coefficients. The effect of changing the film coefficients, therefore, decreases as the thickness of the zone of vaporization increases.

The influence of increasing air velocity on the drying rate curves is to increase the concavity upwards. This same effect could be brought about by decreasing the porosity of the solid and so increasing h_m and decreasing k_m . In this case, the ratios of these coefficients to the corresponding air film coefficients increase in a manner similar to the increase brought about by increasing the air velocity. Thus drying rate curves of non-porous solids should be and are (10) highly concave upward.

The Critical Water Concentration and Rate of Free Water Transfer

One of the most important parts of the drying rate curve is the break between the intervals of constant and falling rate drying at the critical water concentration. During the interval of constant rate drying the atmosphere at the air-solid interface is saturated with water vapor and remains saturated because free water is supplied to the surface of the solid at a rate equal to the rate of drying. The critical water concentration is the minimum water concentration of the solid that will sustain a rate of flow of free water to the surface of the solid equal to the maximum rate of removal of water vapor from the solid under the drying conditions.

At the critical water concentration the solid contains the maximum quantity of bound water, which is a definite weight proportion of the material in the slab. The slab will also contain some free water, which is present in the voids in the solid and is dependent on the amount of material in the solid only insofar as the

amount of material limits the percentage of void space. The concentration of free water is, therefore, best expressed on a volume basis. The critical water concentration is the sum of the concentrations of the bound and free waters:

$$T_{cp.} = Q_z + \frac{F_{cp.}}{D}. \quad (20)$$

Assuming a value of $Q_z = 1.0$ g./g. dry pulp, the free water concentration at the critical point was calculated for each of the pulp runs by means of Equation (20). The results are tabulated in the last column of Table II.

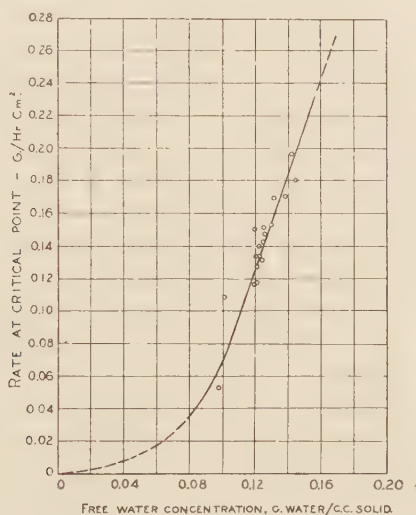


FIG. 13

In Fig. 13, the values of $F_{cp.}$ are plotted against the rate of drying at the critical point. The correlation obtained in Fig. 13 indicates that the rate of free water transfer is, for these pulp slabs, practically independent of thickness and dry density, but depends essentially on the volumetric free water concentration. Sherwood and Comings (12) have previously shown that the critical water concentration depends on the rate of drying.

Attention should be called to the fact that in Runs 115K and 116K the values of $F_{cp.}$ are practically equal in spite of the fact that the corresponding values of $T_{cp.}$ were considerably different, as

shown in Fig. 10. This is a direct check on the fact that free water concentration should be computed on a volume basis.

In spite of the fact that different thicknesses were used in Runs 110K to 114K, the free water concentrations at the critical points of all these runs were equal, as shown in Fig. 9. This indicates that the free water concentration gradient in these slabs was small, otherwise the thicker slabs would have shown higher critical moisture concentrations than the thinner. Although there must have been some free water concentration gradient in the slab when the critical point was reached, the experiments were not precise enough to show it, especially since bound water formed about 60 per cent of the total.

It must be noted that in very thin slabs, the free moisture content at the critical should be noticeably less than for moderately thick slabs. In an infinitesimally thin slab, the critical concentration would equal Q_s .

At present there are not sufficient data to establish the mechanism of free water transfer. The movement of the water probably involves some type of flow analogous to the emptying of horizontal capillary tubes, where the rate is a function of the cross-section area of the flowing liquid. Since the ratio of the cross-section area of the flowing liquid to the drying area is numerically equal to the volumetric free water concentration, Fig. 13 is consistent with this viewpoint.

Shrinkage During Drying

Shrinkage of solids during drying may be divided into two types.

1. Shrinkage due to the collapse of the structure of the solid as free water is removed. The amount of this shrinkage may equal the volume of water removed before the critical water concentration, as found for clay (9), or it may be less than this.

2. Shrinkage due to the shrinking of the material in the solid as the bound water is removed. Such shrinkage occurs after the critical water concentration, and in solids of materials that change in dimension with hygroscopic moisture content.

Both types of shrinkage are illustrated by the data on the shrinkage of the plies comprising the samples used to determine the water concentration gradients of Figs. 4, 6, and 8. The thicknesses of the plies were measured after the plies were separated and before they were dried. The data from groups of plies were averaged and plotted in Fig. 14, as the per cent of original wet thickness versus the average water concentration of the individual plies.

Shrinkage of the material of Run 101K was not appreciable until the free water was removed. The fibers in this sample were rigid and were not drawn together as free water was removed, although this might have occurred if the initial free water content had been sufficient to fill the voids in the sample. The porous structure of the sample permitted air to replace readily the free water removed. The shrinkage occurring after $Q = 1.2$ was most likely due to the shrinkage of the individual fibers as their bound water was removed.

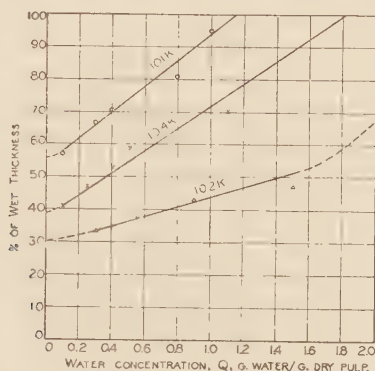


FIG. 14

In Run 102K, most of the shrinkage occurred while the sample still contained free water. The fibers in this sample were short and pliable and as the free water was removed, they were drawn together. After the free water was removed, the shrinkage on a basis of the initial dimensions was less than in the case of Run 101K but on a basis of the thickness of the sample at $Q = 1.1-1.2$, the shrinkage was approximately equal to that of the samples from Run 101K. This indicates that individual fiber shrinkage is approximately the same regardless of the size of the fibers.

Influence of Porosity of Dried Solid in the Zone of Vaporization on the Water Concentration Gradients

Shrinkage of a solid increases its density and decreases its porosity. The amount of shrinkage is a function of the water removed from the solid as shown in Fig. 14, and therefore the porosity of the solid will be least in planes of lowest water concentration. If the material shrinks as the bound water is removed the porosity of the material in the zone of vaporization varies with the

hygroscopic moisture concentration and will increase from the surface to the limit of the zone of vaporization. The coefficient of water vapor diffusion will be smaller at the surface than at the limit of the vaporization zone. By comparing conditions in the vaporization zone of a shrinking slab with those in the vaporization zone of a non-shrinking slab, it follows that, in the case with shrinkage the vapor pressure gradient near the surface will be steeper than that in the case of the non-shrinking solid. As a result of this, the relative humidity and consequently the bound water concentration in the layers nearest the surface are both greater in the shrinking solid than in the non-shrinking solid. In an extreme case, the moisture concentration gradient near the surface may be so steep that the so-called "skin effect" (4) is produced.

This is shown in the water gradient curves of Figs. 4, 6, and 8. The gradient curves change from concave upwards for the porous slab of Run 101K, to concave downwards for the non-porous slab of Run 102K.

Slab 102K can be considered an example of a solid which produces a "skin effect" during drying; that is, a layer of dried material, which is relatively impermeable to water vapor, was formed at the surface of the slab. Lederrer (2) found that the interior of soap slabs retained the original water after several weeks exposure while the exterior became well dried out.

NOMENCLATURE

<i>Symbol</i>	<i>Name</i>	<i>Units</i>
a, b	Constants	
A	Drying Area	cm. ²
c	Specific Heat	
D	Dry Density	g. dry material/cc.
F	Free Water Concentration	g. water/cc.
h_g	Coefficient of Heat Transfer through Air Film	cal./hr., cm. ² , ° C.
h_m	Thermal Conductivity of Solid	cal., cm./hr., cm. ² , ° C.
$\circ J$	Constant	
k_g	Coefficient of Water Vapor Diffusion through Air Film	g./hr., cm. ² , mm. Hg.
k_m	Specific Coefficient of Water Vapor Diffusion through Material in Solid	g., cm./hr., cm. ² , mm. Hg.
K	Overall Coefficient of Water Vapor Diffusion	g./hr., cm. ² , mm. Hg.
L	Distance from Surface to Limit of Zone of Vaporization	cm.

p — Aqueous Vapor Pressure	mm. Hg.
Q — Water Concentration	g. water/g. dry material
r — Latent Heat of Vaporization of Water	cal./g.
S — Rate of Drying	g. water/hr., cm. ²
t — Temperature	° C.
T — Average Water Concentration of Solid	g. water/g. dry material
U — Overall Coefficient of Heat Transfer	cal./hr., cm. ² , ° C.
w_f — Rate of Free Water Transfer	g. water/hr., cm. ²
$\alpha_g = h_g/k_g$	
$\alpha_m = h_m/k_m$	
$C = \alpha_m/\alpha_g$	
θ = time	hours

SUBSCRIPTS

a	Refers to Drying Air
cp.	Refers to Critical Point
g	Refers to Air Film
m	Refers to Material in Solid
s	Refers to Surface of Solid
z	Refers to Limit of Zone of Vaporization
DB	Refers to Dry Bulb Temperature
WB	Refers to Wet Bulb Temperature

LITERATURE CITED

1. Lederrer, Z. f. Angew. Chem., 37, 750 (1924).
2. Lederrer, Seifensieder—Ztg., 51, 779 (1924).
3. Lees and Charlton, Refrigerating Eng., 10, 259 (1924).
4. Lewis, Ind. Eng. Chem., 13, 427 (1921).
5. Lewis, McAdams, Adams, Pulp Paper Mag. (Canada), 25, 122 (1927).
6. Martley, Annals of Applied Biology, 13, 37 (1926).
7. Newman, Trans. Am. Inst. Chem. Eng., 27, 203, 310 (1931).
8. Pukall, Sprecksaal, 59, 367 (1926).
9. Seborg and Stamm, Ind. Eng. Chem., 23, 1271 (1931).
10. Sherwood, Ind. Eng. Chem., 21, 12 (1929).
11. Sherwood, Ind. Eng. Chem., 21, 976 (1929).
12. Sherwood and Comings, Ind. Eng. Chem., 25, 311 (1933).
13. Sherwood and Comings, Trans. Am. Inst. Ch. E., Dec. 1932.
14. Troop and Wheeler, J. Cer. Soc. (Eng.), 27, 303 (1927).
15. Tuttle, J. Frank. Inst., 200, 609 (1925).
16. Sherwood, Ind. Eng. Chem., 22, 132 (1930).

DISCUSSION

ALBERT B. NEWMAN (written): In regard to the division of the water content of a hygroscopic solid into two classes, bound and free, I believe that the authors have a sound basis. This is confirmed by the shape of the vapor pressure: water content curve of silica gel which is reproduced in most books on colloid chemistry. This curve shows a break which is generally attributed to a transition from bound to free water. However, in the case of a highly adsorbent solid like silica gel, Dr. McCready's assumption that bound water is transferred through the solid only as a vapor seems arbitrary, inasmuch as most of the possible water content is bound. Possibly a better way of handling bound water would be the application of some kind of "activity" concept such as has been successfully introduced into chemical thermodynamics by G. N. Lewis. In the present case, instead of using the actual water concentration in our diffusion equations, we would use a fictitious concentration proportional to the vapor pressure corresponding to actual concentration. . . .

D. W. MCCREADY AND W. L. MCCABE (written): Professor Newman notes the arbitrariness of the assumption that bound water (defined as the moisture content of the solid that does not exert its full vapor pressure) can only be transferred as vapor under drying conditions. The authors recognize the fact that this is a simplifying assumption, and is to be used only in the absence of experimental data showing definitely the relation between the moisture concentration corresponding to maximum bound water and the concentration corresponding to a definite slowing down of the diffusion of liquid water. The assumption is suggested by the probability that any forces that tend to suppress the vapor pressure of the water should also act to inhibit its flow by liquid diffusion.

The suggestion that the use of a fictitious concentration proportional to the vapor pressure corresponding to the actual concentration is interesting, and when more data are available of sufficient accuracy to test the utility of such a unit, this idea may prove useful. . . .

